



PATENT SPECIFICATION

DRAWINGS ATTACHED

874,762

Date of Application and filing Complete Specification: Oct. 28, 1957.

No. 33568/57.

Application made in Germany on Oct. 27, 1956.

Complete Specification Published: Aug. 10, 1961.

Index at acceptance:—Class 2(6), P4C(3:7:8B:8C:9:12A:13A:13C:14A:16A:16B:16C:17:18:20B:20D1:20D3), P4D3B(1:3), P4K4.

International Classification:—C08f.

COMPLETE SPECIFICATION

Flameproofing Coating Compositions

5 We, FARBERWERKE HOECHST AKTIENGESELLSCHAFT vormals Meister Lucius & Brüning, a body corporate recognised under German Law, of Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 It is known to use as binding agents in flameproofing coating compositions copolymers of vinyl chloride and vinylidene chloride, chlorinated polyethylene and polyacrylates, and also resinous condensation products of urea and formaldehyde which are further condensed when the coating has been formed. These binding agents in admixture with organic-bubble-forming substances and advantageously with ammonium salts, such as mono-ammonium phosphate, yield flameproof coatings which produce a foamed layer when heated. Attempts have been made to use as binding agents for such flameproofing coating compositions other film-forming polymers, especially dispersions of polyvinyl esters, for example, of polyvinyl acetate, polyvinyl propionate and copolymers. However, it has been found that these dispersions impair to a greater or less degree the foam-forming capacity of the foam-forming substances and yield compositions having an inadequate flameproofing effect, so that these dispersions have been regarded as unsuitable for flameproofing compositions. Attempts to improve the foaming-forming capacity of these flameproofing coating compositions failed owing to the sensitivity to electrolytes of the aforesaid dispersions, since the salts necessary to improve the compositions in the above respect, for example, mono-ammonium phosphate, are electrolytes and bring about coagulation of the dispersions.

45 The present invention is based on the observation that excellent flameproofing compositions containing at least one water-soluble electrolytic flameproofing agent and, if desired,

pigments, can be obtained by using as binding agents aqueous polyvinyl ester dispersions stable to electrolytes that is to say dispersions which are not coagulated by electrolytes, for example, aqueous dispersions of polyvinyl acetate, polyvinyl propionate and of copolymers of vinyl acetate and vinyl propionate obtained as described in Specification No. 38,249/57 (Serial No. 871,254). The resulting flameproofing coating compositions dry without producing any odour to form films without the aid of heat.

As polyvinyl ester dispersions stable to electrolytes there may be used, for example, those containing emulsifying agents or stabilizers that are highly stable to electrolytes. Examples of such emulsifying agents and stabilizers are water-soluble derivatives of cellulose or of starch, such as oxyalkylated cellulose in which the alkyl groups contain 1—4 carbon atoms, or polyvinyl-pyrrolidone or polyacrylic acid amide.

70 The flameproofing coating compositions of this invention yield coatings having an excellent flameproofing effect and capable of forming foamed layers, when the composition contains an organic bubble-forming agent. As water-soluble electrolytic flameproofing agents suitable for incorporation in the coating compositions of this invention, and which are advantageously incorporated in a proportion amounting to about 10% to about 40% by weight, calculated on the coating composition, there may be used, for example, mono-ammonium or diammonium phosphate, tri-sodium phosphate, potassium mono- or di-phosphate, ammonium sulphate, ammonium sulphamate, ammonium bromide, ammonium chloride, ammonium borate, boric acid, sodium tetraborate, sodium pentaborate hydrate, sodium acetate, zinc chloride, aluminium chloride or mixtures of two or more of these substances.

Organic bubble-forming substances may also be incorporated in the compositions, and 90

- advantageously added in a proportion amounting to about 15% to about 50% by weight, calculated on the composition. Examples of organic bubble-forming substances are dicyandiamide, dicyandiamide phosphate, pentaerythrite, sorbitol, mannitol, hexitol, completely condensed urea-formaldehyde resins, albumin, starch or mixtures of two or more of these substances.
- 10 The polyvinyl ester dispersion may also contain one or more plasticisers in a proportion amounting to about 5 to about 50%, and preferably 10 to 20%, calculated on the weight of the polymer. As plasticisers there
- 15 may be used, for example, dibutyl phthalate, dimethylglycol phthalate (diester of methylglycol with phthalic acid), dimethyl-thianthrene, benzyl butyl adipate, ethyl hexyl sebacate or triethyl citrate. Especially suitable
- 20 are flame-inhibiting plasticisers such as trichlorethyl phosphate, diphenyl cresyl phosphate, triphenyl phosphate, tricresyl phosphate, tetrachlorophthalic acid dibutyl ester, phthalic acid chlorethyl di-ester and phthalic acid chlorobutyl di-ester or mixtures of two or
- 25 more of these plasticisers. If desired, there may also be added to the dispersions up to 20%, calculated on the coating composition, of one or more organic flame-inhibiting agents, such as chloroparaffin waxes containing 50 to 70% of chlorine, or other chlorinated hydrocarbons, for example chlorinated diphenyl, so that the binding agent also becomes an effective flameproofing component of the dispersion.
- The dispersions may also contain about 5 to about 50%, calculated on the coating composition, of one or more fungicides or insecticides, such as sodium fluoride, potassium fluoride, ammonium fluoride, sodium bifluoride, potassium bifluoride, ammonium bifluoride, magnesium silicofluoride, zinc silicofluoride, mercuric chloride, arsenic acid, potassium or sodium arsenate, copper sulphate, sodium pentachlorophenolate, dinitrophenol, dinitroresol or the like.
- There may also be incorporated with the coating compositions about 2 to about 10%, calculated on the composition, of pigments such as titanium dioxide, antimony trioxide, red iron oxide, yellow iron oxide, green chromium oxide, and in appropriate cases mixtures of pigments. The pigmented coating compositions are homogeneous products which are ready for use and withstand storage.
- Especially suitable are flameproofing coating compositions which comprise a polyvinyl acetate dispersion stable to electrolytes in admixture with about 15 to about 25% by weight of mono-ammonium phosphate as a flameproofing salt and about 20% by weight of dicyandiamide and about 10 to about 15% by weight of pentaerythrite as a bubble-forming mixture, all the percentages being calculated on the coating composition.
- The following Examples numbered 2(a), 4(a), 6(a) and 8(a) illustrate the invention, the others being given for the sake of comparison only:

EXAMPLES 1 AND 2: FLAMEPROOFING COATING COMPOSITIONS NOT FORMING FOAMED LAYERS.

All quantities are percentages by weight:

Examples	1		2	
	(a)	(b)	(a)	(b)
Polyvinyl acetate dispersion not stable to electrolytes (content of solid substance 55%)	—	30	—	30
Electrolyte-stable polyvinyl acetate dispersion (content of solid substance 55%) (§)	30	—	30	—
Magnesium ammonium phosphate	40	40	—	—
Mono-ammonium phosphate	—	—	40	40
Pigment(*)	— ⁽¹⁾	— ⁽¹⁾	— ⁽¹⁾	— ⁽¹⁾
Water	30	30	30	30
Stability of the dispersion	stable	stable	stable	coagulates
Flameproofing effect	small	small	very good	

(*) For example, titanium dioxide, antimony trioxide, red iron oxide, yellow iron oxide, green chromium oxide.

(§) Produced by polymerising vinyl acetate in the presence of 2% of hydroxyethyl cellulose as stabiliser.

⁽¹⁾ May contain a pigment for decorative purposes or for identifying the flameproof coating.

Compositions containing
no flameproofing agent

	3		4		5		6		7		8		I		II		III	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
Polyvinyl acetate dispersion not stable to electrolytes (content of solid substance 55%)	—	45	—	45	—	25	—	25	—	20	—	20	—	45	—	25	—	20
Electrolyte-stable polyvinyl acetate dispersion (content of solid substance 55%) stabilized as in example 1	45	—	45	—	25	—	25	—	20	—	20	—	45	—	25	—	20	—
Magnesium ammonium phosphate	20	20	—	—	20	—	—	—	20	20	—	—	—	—	—	—	—	—
Mono-ammonium phosphate	—	—	20	20	—	—	20	20	—	—	20	20	—	—	—	—	—	—
Dicyandiamide	9	9	9	9	15	15	15	15	17	17	17	17	19	19	25	25	27	27
Pentaerythrite	6	6	6	6	12	12	12	12	13	13	13	13	16	16	22	22	23	23
Starch	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Pigment	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Water	15	15	15	15	23	23	23	23	25	25	25	25	15	15	23	23	25	25
Foamed layer protection	weak	—	good	—	medium	—	very good	—	medium	—	very good	—	weak	—	weak	—	weak	—
Flameproofing effect	small	—	good	—	small	—	very good	—	medium	—	very good	—	none	—	none	—	none	—
				Dispersion coagulates			Dispersion coagulates				Dispersion coagulates							

- The flameproofing coating compositions (a) of Examples 6 and 8, which possess a very good flameproofing effect, have the ranges of efficiency values shown in the accompanying drawing, as determined by the official test according to Din 4102 of the German Federal Republic. To satisfy this test the final loss in weight of the test object must not exceed 15% after exposure to flames for 15 minutes. In the drawing the ordinates represent the percentage loss in weight and the abscissae the quantity in grams of active substance (flameproofing salt + organic bubble-forming substances) per square metre of treated surface. The curve B1 shows the values for composition (a) of Example 8 and curve B2 those for composition (a) of Example 6.
- WHAT WE CLAIM IS:—
1. A flameproofing coating composition which consists of an aqueous polyvinyl ester dispersion which is not coagulated by electrolytes and contains at least one water-soluble electrolytic flameproofing agent.
 2. A composition as claimed in Claim 1, wherein the flameproofing agent is an ammonium salt.
 3. A composition as claimed in Claim 2, wherein the ammonium salt is mono-ammonium phosphate, diammonium phosphate, ammonium sulphate, ammonium sulphamate, ammonium bromide, ammonium chloride or ammonium borate.
 4. A composition as claimed in Claim 1, wherein the flameproofing agent is trisodium phosphate, potassium mono- or di-phosphate, boric acid, sodium tetraborate, sodium pentaborate hydrate, sodium acetate, zinc chloride or aluminium chloride.
 5. A composition as claimed in any one of claims 1—4, wherein the proportion of the flameproofing agent is within the range of about 10 to about 40 per cent calculated on the weight of the composition.
 6. A composition as claimed in any one of Claims 1—5, which also contains an organic bubble-forming substance.
 7. A composition as claimed in Claim 6, wherein the bubble-forming substance is dicyandiamide, dicyandiamide phosphate, pentaerythrite, sorbitol, mannitol, hexitol, a completely condensed urea-formaldehyde resin, albumin or starch.
 8. A composition as claimed in Claim 6 or 7, wherein the proportion of the bubble-forming substance is within the range of about 15 to about 50 per cent calculated on the weight of the composition.
 9. A flameproofing coating composition which consists of a polyvinyl ester dispersions which is stable to electrolytes and contains about 15—25% of monoammonium phosphate, about 10—20% of dicyandiamide and about 10—15% of pentaerythrite, the percentages being calculated on the weight of the composition.
 10. A composition as claimed in any one of claims 1—9, which also contains up to 20 per cent of its weight of an organic flameproofing agent.
 11. A composition as claimed in claim 10, wherein the said organic flameproofing agent is a chloroparaffin wax containing 50 to 70 per cent of chlorine.
 12. A composition as claimed in any one of claims 1—11, wherein the polyvinyl ester dispersion contains an emulsifying agent or stabiliser stable to electrolytes.
 13. A composition as claimed in claim 12, wherein the emulsifying agent or stabiliser is polyvinyl-pyrrolidone, polyacrylic acid amide, or a water-soluble derivative of cellulose or of starch.
 14. A composition as claimed in any one of claims 1—13, wherein the said dispersion is a polyvinyl acetate dispersion.
 15. A composition as claimed in any one of claims 1—13, wherein the said dispersion is a polyvinyl propionate dispersion.
 16. A composition as claimed in any one of claims 1—13, wherein the said dispersion is a dispersion of a copolymer of vinyl acetate and vinyl propionate.
 17. A composition as claimed in any one of claims 1—16, which also contains a plasticiser in a proportion within the range of about 5 to about 50 per cent calculated on the weight of the polyvinyl ester.
 18. A composition as claimed in any one of claims 1—17, which also contains one or more pigments in a proportion with the range of about 2 to about 10 per cent calculated on the weight of the composition.
 19. A composition as claimed in any one of claims 1—18, which also contains one or more fungicides and/or insecticides in a proportion within the range of about 5 to about 50 per cent calculated on the composition.
 20. A flameproofing coating composition having substantially the composition given in any one of Examples 2(a), 4(a), 6(a) and 8(a).

ABEL & IMRAY,
Agents for the Applicants,
Quality House, Quality Court,
Chancery Lane, London, W.C.2.

874762 COMPLETE SPECIFICATION

1. SHEET This drawing is a reproduction of
the Original on a reduced scale

